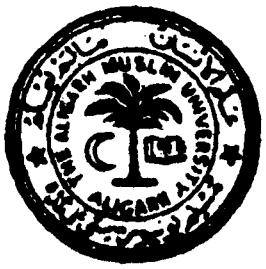

PHYSICO-CHEMICAL STUDIES ON WATER-POLLUTANTS.

DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE AWARD OF THE DEGREE OF

Master of Philosophy

IN

CHEMISTRY

Under the Supervision of

Dr. ANEES AHMAD

By

QASIM ULLAH

DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH (INDIA)

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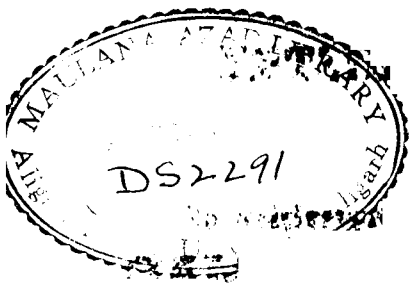
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DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
A L I G A R H—202 002

PHONE : (0571) 25515

March, 9. 1994
Dated.....

TO WHOM IT MAY CONCERN

This is to certify that the work embodied in this dissertation entitled **"PHYSICO-CHEMICAL STUDIES ON WATER-POLLUTANTS"**, is the original contribution of the candidate and is suitable for submission for the award of M.Phil. degree in Chemistry of Aligarh Muslim University, Aligarh

(Dr. Anees Ahmad)
Supervisor

Dedicated to my

Parents

CONTENTS

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Qasim ullah
(QASIM ULLAH)

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CHAPTER I

INTRODUCTION

Environmental pollution [1] has been defined as the unfavorable alternation of our surroundings by industrialization or by other human activities. A substance is called a pollutant provided it interfere with health, comfort, amenities or property values of people. Generally a pollutant is introduced into the environment as sewage, waste, accidental discharge or as a by-product of manufacturing processes. It is also introduced into the environment as compounds used to protect plants and animals.

Pollutants are of different kinds in surroundings which are found in the form of liquid, gas or solid. On these bases they may be broadly classified into following classes - (a) Inorganic Pollutants and, (b) Organic Pollutants.

Table 1.1

SOME COMMON INORGANIC POLLUTANTS

S. No.	Pollutants	Sources	Nature of Pollution	Remarks
1	2	3	4	5
1.	Carbon monooxide	Incomplete combustion of Carbon	Air	Leads to unconsciousness (300 ppm) and ultimately death (750 ppm)
2.	Carbon dioxide	Combustion of Carbon from various sources	Air	Excessive CO_2 may lead to green house effect
3.	Sulphur dioxide	Oil refineries, thermal stations, fertilizer and sulphuric acid plants, petroleum industries.	Air, Water	Damage Nucleic acids

(Continued on next page)

4.	Hydrogen Sulphide	Decomposition of organic matter, sewage, Petroleum industries, and refineries.	Air, Water	Respiratory irritations in man, corrosion of materials, affects growing tips of sensitive plants.
5.	Nitrogen Oxides	Combustion Processes in air exhausts of automobiles, explosive industries.	Air	Chronic respiratory ailments
6.	Lead	Exhausts of automobiles, Jet engines artificial satellites.	Air, Water, Soil.	Lead compounds coagulated body proteins and seriously disrupt metabolic activities.
7.	Zn, Hg, Cu, Ni, Cd, Pb.	Various industrial discharges	Air, Water, Soil.	Minamata type of disease (Japan)
8.	Fluorides	Industrial discharge	Water	Excess of F^- leads to blackening of enamel or teeth.

(Continued on next page)

9.	Phosphates	Mainly from sewage of detergents	Water	Oxidative degradation of organic matter which consumes O_2
10.	Nitrates	Sewage	Water	dissolved, algal boom, eutrophication of lakes, hamper fishing, navigation, irrigation and hydroelectric power.
11.	Arsenic	Industrial Waste liquors	Water, Soil.	Arsenic poisoning
12.	Cl_2, HCl	Industrial discharge	Air Water	Respiratory ailments
13.	HCN and Cyanides	Steel plants, electroplating	Air, Water, Soil.	Stops breathing, blood poisoning
14.	NH_3 and ammonium compounds	Fertilizers industries biodegradation of proteinaceous materials.	Air, Water, Soil	Respiratory ailments, disrupt metabolic activities
15.	Chromium	Effluent of planting and other metal processing factories.	Water	Disrupt metabolic activities (70.05 ppm)

Table 1.2

SOME COMMON ORGANIC POLLUTANTS

S. No.	Pollutants	Sources	Nature of Pollution	Remarks
1.	Organochlorine Compounds e.g.DDT,BHC	Pesticides	Air,Water Soil	Deposition in fat tissues, suspected carcinogens
2.	Organophosphorus e.g. Malathion, Monochrotophos	do	do	Carcinogen
3.	Carbamates e.g. Isolan, Dimetan,Pyramat	do	do	Inhibitor of cholin esterase
4.	Thiocyanates e.g. Lethane 60, Lethane 384,	do	do	Interferes with cellular respiration and metabolism

(Continued on next page)

5.	Formamidines e.g. Chlordimeform, Amitraz	do	do	Carcinogen
6.	Organo Sulphurs e.g. Tetradifon, Genite, Ovex	do	do	Comparatively less toxic and affects mites more
7.	Dinitrophencls e.g. Dinitrocresol, Morocide, Karathane	do	do	Causes rapid loss in weight
8.	Organotins e.g. Plictran	do	do	Inhibition of Oxidative Phosphorylation

(Continued on next page)

9.	Organics containing tertiary nitrogen			
	Acridine	do	do	Carcinogen
	Amitrol	do	do	do
	Atrazine	do	do	do
	Azobenzene	do	do	Liver Injury
	Bavistin	do	do	Carcenogen
	Calixin	do	do	do
	2,4, Lutidine	Coal, Petro - leum, degrada- tion of Proteinaceous Materials, Bone oil.	do	CNS depression, irrita- tion of skin and respira- tory tract G.I. distur- bances Kidney and liver damage and suspected carcinogen.
	2,6, Lutidine	do	do	do
	Nicotinic acid	Tobacco	do	do
	Quinoline	Coaltar	do	do
	Picloram	Pesticide	do	Carcinogen
	Trimethyl amine	Decay of fish.	Water	do

Environmental pollution is the burning problem of modern life. Therefore, a number of books [2-9] have been written and international symposia [10-16] have been organized on the subject. In developing countries like India, there is an immense need of simple and inexpensive methods for pollution monitoring and control. Therefor, an attempt have been made to develop simple and sensitive techniques for the detection and determination of these pollutants. Analytical chemistry plays a very important role in both dealing and controlling environmental pollution. It can be thought as comprising of two branches, qualitative and quantitative. Qualitative analysis deals with finding what constituent or constituents are in analytical sample, and quantitative analysis deals with the determination of how much of a given substance is in the sample. With today's instrumentation and with a large variety of chemical measurements available, specificity or sufficient selectivity can often be achieved so that the quantitative measurement serves as a

qualitative measurements.

Adsorption and ion-exchange are the two important conception in analytical chemistry since the solid-liquid interactions have always been of interest because of their diversity and immense applications. Interactions between the components of liquids or solutions and surfaces of the solids make, in a wide variety of ways, a momentous contribution to our everyday life. Its importance in the petroleum, chemical and pharmaceutical industries is well established. However, recent activities in biotechnology, medicine, biomedical, biochemical, environmental and polymer engineering have broadened the usefulness of processes. Similarly, ion-exchange is one of the most versatile analytical technique in Separation Science. Various applications of ion-exchange procedures are in the field of heterogeneous catalysis, radiochemical analysis, solid electrolytes, inorganic ion-exchange membranes, environmental studies, ion-selective electrodes and intercalation compounds.

A. ADSORPTION:

Adsorption may be defined as "the phenomenon of higher concentration of any molecular species at the surface than in the bulk of a solid (or a liquid) is known as adsorption.

Adsorption [17] can be distinguished carefully from absorption. The latter term implies that a substance is uniformly distributed throughout the body of a solid or liquid. The solid that takes up a gas or vapour or a solute from a solution, is called the adsorbent, while the gas or the solute, which is held to the surface of the solid, is called the adsorbate.

Mc Bain [17] suggested that the term sorption should be used to describe a process in which both absorption and adsorption take place simultaneously.

The phenomenon of adsorption, is also known as surface phenomenon, has been known since 1773 when Scheele [17] discovered the uptake of gases by charcoal. Sometimes the adsorption can be classified as Physical adsorption or physisorption

and chemical adsorption or chemisorption. The former is also known as Vander waal's adsorption in which gaseous molecules are held to the surface of an adsorbent by physical or Vander Waal's forces i.e. the forces of molecular attraction. Physical adsorption of a gas is accompanied by a low heat of adsorption which is of the same order as the heat of liquefaction of gas.

Chemisorption, in which the gaseous molecules are more or less completely dissociated into atoms which combine with the surface atoms of the adsorbent by valency forces i.e. by the process of electron sharing as in the formation of chemical compounds. Chemisorption is accompanied by evolution of a large amount of heat. Chemisorption of hydrogen on Nickel is represented as below [18].

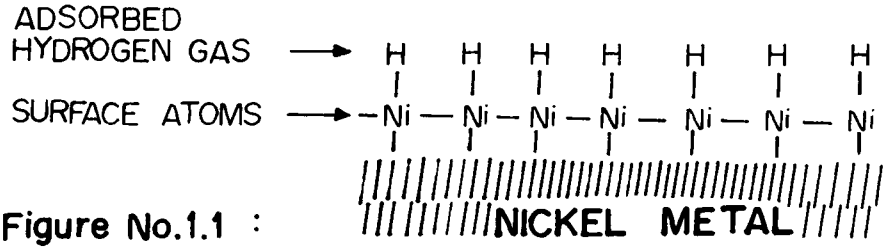

Figure No.1.1 :

In chemisorption, the surface enters into reactions as a catalyst. This type of catalysis, called

heterogeneous catalysis, is understandable only on the basis of some of the informations deduced in adsorption studies. The photo electron spectroscopy (ESCA) can be applied to reveal some of the bonding properties of the adsorbed species. In surface studies this is normally referred as photoemission spectroscopy. Adsorption is essentially a phenomenon of separating surface and the interfacial tension [19]. It is generally governed by the thermodynamic relation.

$$\Delta G = \Delta H - T \Delta S \qquad (1)$$

ΔG, ΔH and ΔS are taken, respectively, as the free Energy, heat and entropy changes in the process. The Process of adsorption is generally exothermic but endothermic process have also been reported in case of large ionic-miceller system such as those of dyes in solution.

The reverse process (i.e. desorption) measures the resistance of the systems to change, and manifests itself as a binding force between the adsorbate and adsorbent. The binding forces involved may be of several types, such as vander

Waal's Ion exchange, covalent bond formation and hydrogen bonding, depending on the nature of the substrate, surface and the adsorbate.

The surface structure of a solid is controlled to a large extent, by the underlying bulk structure which, in turn, is defined by chemical composition and crystal structure. The various surface groups on the common polar adsorbents may ionize in the presence of water or similar solvents leaving a net charge or so called zeta-potential, on the surface of the adsorbent. This surface charge has been claimed by many workers [20,21] to have an important effect on the sorptive properties of an adsorbent, especially where ion-exchange plays an important role.

Adsorption Isotherms: Most of the studies on adsorption from solution have been concerned with equilibrium conditions, and predominantly with the adsorption isotherms. An adsorption isotherm describes the equilibrium relationship between the adsorbed and unadsorbed sample, at a given temperature. It is a plot of the concentration of

"x" in the unadsorbed phase. The interest in these isotherms lies in the amount of information they can yield, viz., identification of the adsorption mechanism, heat of adsorption, specific surface area of the porous solid, diagnosis of the orientation of the solute molecules at the surface, and its degree of self associations.

The earlier attempts [22] of classification of isotherms have served for quite a long time. Four types of isotherms are identified on the basis of the shape of the initial part of the isotherms. This classification of isotherms had been reported and theoretically explained by Giles et al [20,23] on the basis of solid solution interface. various shapes of the isotherms considered are shown in Fig. 1.2, and can be characterized as follows:

(i) Langmuir or L-type isotherms

(ii) S-type isotherms

(iii) High affinity or H-type isotherms, and

(iv) Constant partition or C-type isotherms.

The L-type isotherms are most common. They are characterized by an initial region which is

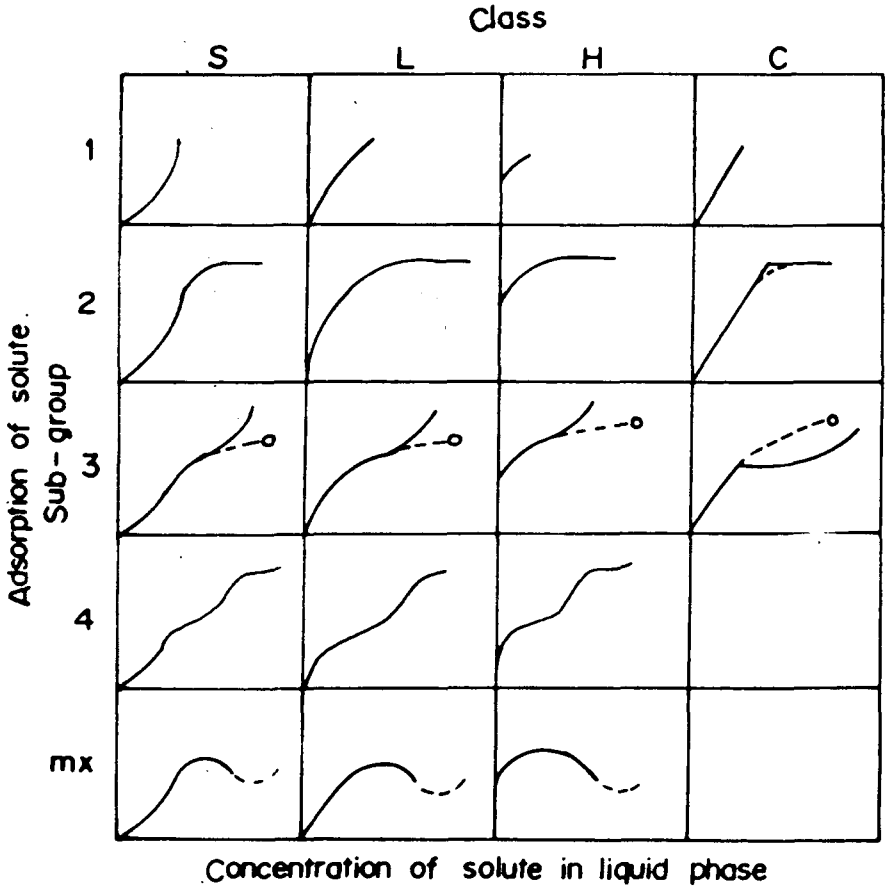

FIGURE 1.2 : Classification of isotherms shape (Giles etal, 1960, 1974)

concave to the concentration axis. They are obtained when there is no strong competition from the solvent for sites on the surface. The curves refer to those cases in which the most active sites are initially covered, but the case with which adsorption takes place decreases until a monolayer is completed.

For the S-type Isotherms the initial region is convex to the concentration axis which is frequently followed by a point of inflection leading to an S-shaped curve. These isotherms indicates that

i) The solvent is strongly adsorbed

ii) There is strong intermolecular attraction within the adsorbed layer, and

iii) The adsorbate is monofunctional.

The second condition is most likely obtained, if the major axis of the adsorbed molecules is perpendicular to the surface. By a monofunctional adsorbate we mean here that the molecule has a single point of strong attachment in an aromatic system or an aliphatic system of more than five

carbon atoms. Further, the adsorbate is not miceller. In many cases, the S-curve indicates a 'cooperative adsorption' with solute molecules tending to be adsorbed, packed in rows or clusters.

The H-curve occurs when there is a high affinity between the adsorbate and adsorbent, which is shown even in very dilute solution. Thus, it can result from the chemisorption or from the adsorption of polymers or ionic micelles, though other special cases are known.

Finally the C-type Isotherm has an initial linear portion which indicates a constant partition of the solute between the solution and the adsorbent and occurs with the microporous adsorbents.

The isotherms have a great utility in diagnosing the mechanism of adsorption, and also in distinguishing the probable configuration of the adsorbed molecules [20]. Thus, S-curve indicates a vertical orientation, L-curve shows the flat orientation and strong intermolecular interaction, while H-type isotherm is assumed to be typical of

sample micelle formation. However, such a generalization needs great care, as many other factors also contribute to the isotherm's shape [24].

The adsorbents which have been commonly studied earlier are fly ash [25-30], peat [31-36] clays [37,38] alumina bauxite [39], wool-astonite [40,41], and sludge [42-48]. Some other adsorbents have been proved quite useful viz. alumina, silica, carbon and cellulose [49]. In addition to these, some adsorption studies have also been reported on tin oxide, titanium oxide, thorium oxide and zirconium oxide. [50]

Mechanism of adsorption:

Although adsorption from solution by solids is of great practical importance and a vast number of papers have been published. Much of the early work was concerned with relatively dilute solutions, and interpretation of the isotherms was not unreasonably analogous to that used for adsorption from the gas phase and experimental results were fitted to equations of the Langmuir and Freundlich

types. The role of solvent and its competition with the solute for surfaces sites has now become recognized as an important factor, particularly as a result of a large number of studies on the adsorption from binary liquid mixtures and their thermodynamic analysis.

The interaction between the surface and adsorbed species may be either chemical or physical. Several types of bonding can be identified as follows [51]:

(1) **Chemical adsorption (chemisorption)-** stearic acid from benzene solution on metal powders.

(2) **Hydrogen bonding** - long-chain alcohols from hydrocarbon solution on dry oxide surfaces.

(3) **Hydrophobic bonding-** association of hydro carbon chains to "escape" from an aqueous environment, e.g., acids on polystyrene

(4) **Vander Waal's forces.**

The net interaction of an adsorbate molecule with a surface might involve more than one type of interaction, depending on the chemical structure of both components.

The most favoured approach to an investigation of the adsorption mechanism is a study of the isotherm [51]. The important aspects are (a) the rate of adsorption (b) the shape of the isotherms (c) the significance of the plateau found in many isotherms (d) the extent of solvent adsorption, (e) whether the adsorption is mono molecular or extends over several layers. (f) the orientation of the adsorbed molecules. (g) the effect of temperature. (h) the nature of the interaction between adsorbate and adsorbent.

Some Recent Studies on the Adsorption Behaviour of Saw Dust

Many workers studied adsorption behaviour of heavy metals on saw dust which are summerised as follows:

(1) **Removal of chromium (vi)-** Singh, D.K. Mishra et al [52] used saw dust for the removal of Cr^{6+} from aqueous solution by using column packed. The removal of Cr^{6+} was max. at pH-2.

(2) **Removal of Lead and Copper Ions:** Aval,G. Motedaiyen [53] have studied the adsorption

behaviour of Pb^{++} & Cu^{++} on saw dust column. The concentration. of these ions (as measured via at absorption spectroscopy) could be reduced to <1ppm

Chung. Yongsoon et. al. [54] have also studied the adsorption behaviour of heavy metal ions on saw dust column.

(3) **Determination of Copper in industrial effluents and Receiving Water and Its Removal** Begum, Shakila [55] estimated Cu by using saw dust in effluents as well as in water with the help of Langmuir adsorption equation. The maximum adsorption capacity of the adsorbent increased with temperature between 30-50 °C.

(4) **Adsorption of Cu^{++}**: Vaishya & Prasad [56], have studied the adsorption of Cu^{++} on saw dust of Bassia latifollia without any pH adjustment. The sorption equilibrium data were modeled by both Freundlich and Langmuir isotherm. Copper, removal was observed and it was found that the maximum adsorption take place at pH 7.3.

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CHAPTER II

INTRODUCTION

The environmental pollution in general and water pollution in particular is the burning problem of modern life. Therefore, a number of books [1-6] have been written and international symposia have been organized on the subject. Water is polluted by the industrial waste and effluents. Industrial waste includes heavy metals such as Zn, Cd, Hg, Cu etc. and other impurities.

Zinc is discharged into the waste streams of many industries such as steel works with galvanizing lines, zinc and brass metals works, zinc and brass plating, viscose rayon, yarn and fiber production, ground wood pulp production and news print paper production. The zinc salts are also used in the pigment industries. The safety limit of zinc for aquatic life is given as 5 mg/L.

Cadmium is introduced into aquatic system through discharge of their untreated effluents into various water bodies by industrial process such as electroplating process. Cd^{++} has been proven to be a non essential and non beneficial elements. It

causes a number of acute and chronic disorders, causing cancer of various parts of the body, the fatal 'itai-itai' disease, cyanosis, anemia, weakening of bones etc. [7]. Therefore, the industrial effluents/ waste waters containing cadmium should be treated to eliminate/reduced the cd-contents prior to their discharge into the receiving water bodies. A number of process are known which are employed for the removal of heavy metals. The major of them are neutralization, precipitation, adsorption, ion-exchange etc. Adsorption process using activated carbon has been a popular choice in developed countries like U.S.A. but the high cost of activated carbon limits its use in the developed nations only.

The adsorption phenomenon has still been found economically appealing for the removal of toxic metals from waste waters, by choosing some adsorbents under optimum operation conditions. Several adsorbents have been used earlier for treatment of these metal ions (Zn^{++}, Cd^{++}). It has been reported that some aquatic plants [8-11],

agricultural by products [12], waste tea leaves [13], and sawdust [14], have the capacity to adsorb and accumulated heavy metals.

The study of the feasibility of these metal-ions (Zn^{++} Cd^{++}), by sawdust, an unconventional adsorbent is describe here. Much attention has been paid to optimizes the effective abatement conditions in a cost effective fashion. Saw dust, one of the cheapest and abundantly available adsorbent has been tried for the uptake of these metals from aqueous solution. The effect of equilibrium time, pH, temperature, concentration, dose and salinity on the removal of these metals by saw dust have been studies. The adsorption isotherm and the probable mechanism have been explained. The appropriate thermodynamic parameter, viz., change in free energy, entropy and enthalpy have been calculated and described here.

MATERIAL AND METHODS

1.1. Adsorbent:

Saw dust was used as an adsorbent for the removal of these metal-ions from aqueous solution. It was collected from the timber workshop situated near the university campus. Saw dust was treated with HCl and washed with distilled water thoroughly to clean the adhering dirt, and finally dried in an air oven at 100^{O}C and then used.

1.2 Adsorbent solution:

The stock solution of metal-ions was prepared (.005M) by dissolving their corresponding salts in distilled water and standardized complexometrically with EDTA (disodium salt) using EBT (Eriochrome Black-T). All other reagents used were of analytical grade.

1.3. Batch Adsorption Studies: Batch adsorption experiments were carried out by shaking 0.5 gm of the saw dust with 50 ml aqueous solution of metal ions solution of desired concentration at various pH and at different temperatures (22^{O}C to 60^{O}C) in different stoppered bottles for different

retention times using a temperature controlled shaker. At the end of the predetermined time interval the adsorbent was removed by filtration and the equilibrium concentration was estimated with EDTA. Blanks were also prepared to find out the adsorption on to the internal surface of the bottles, if any. The effect of pH on the adsorption phenomenon was studied by adding either 1.0 N HCl or NaOH in metal-ions solution.

To study the effect of salinity on the removal of these metal ions (Zn^{++}, Cd^{++}), the experiment was also conducted in presence of NaCl at $40^{O}C$ only. The concentration of the NaCl was maintained at 0.1 M by adding 5 ml of a 1.0 M NaCl stock solution.

1.4 Adsorption Model:

To quantify, the adsorption capacity of saw dust for the removal of metal-ions solutions from water, the Langmuir and Freundlich equations were applied.

a) Langmuir Model: Langmuir proposed the following model:

$$Ce/Am = 1/K\ 1/b + (1/b)\ Ce \qquad (1)$$

where 'Ce' is the equilibrium concentration (mole/l) and 'Am' is the amount adsorbed per specified amount of adsorbent (mg/g). 'K' is the equilibrium constant and 'b' is the amount of adsorbate required to form a monolayer, Hence, a plot of Ce/Am vs. Ce should be a straight line with a slope 1/b and intercept as 1/Kb.

b) Freundlich Model: According to this model

$$Am = K.Ce^{1/n}$$

$$\text{or } \ln (Am) = \ln K + 1/n\ [\ln (Ce)] \qquad (2)$$

where all the terms have the usual significance and 'n' is an empirical constant. Thus a plot of ln (Am) Vs. ln (Ce) should be a straight line with a slope '1/n' and intercept ln K. This model deals with the multilayer adsorption of the substance on the adsorbet . The points indicate the observed data and the line corresponds to the fitted data.

A computer simulation technique have been applied to fit the Freundlich and Langmuir equations, for the adsorption data. The coefficients of least square fitting to a straight

link (R) were computed for these two models.

The thermodynamics parameter ΔG, ΔH and ΔS. were computed from the equations given below and listed in table. The free energy change (ΔG) was calculated from the relations,

$$\Delta G = - RT \ln K \quad (3)$$

Similarly, the enthalpy change $\triangle H$ between 22 to $60^{\circ}C$ was computed from the following equation:

$$\ln K = - \Delta H/RT + C \quad (4)$$

and the entropy change was calculated from the equation.

$$\triangle G = \Delta H - T \Delta S \quad (5)$$

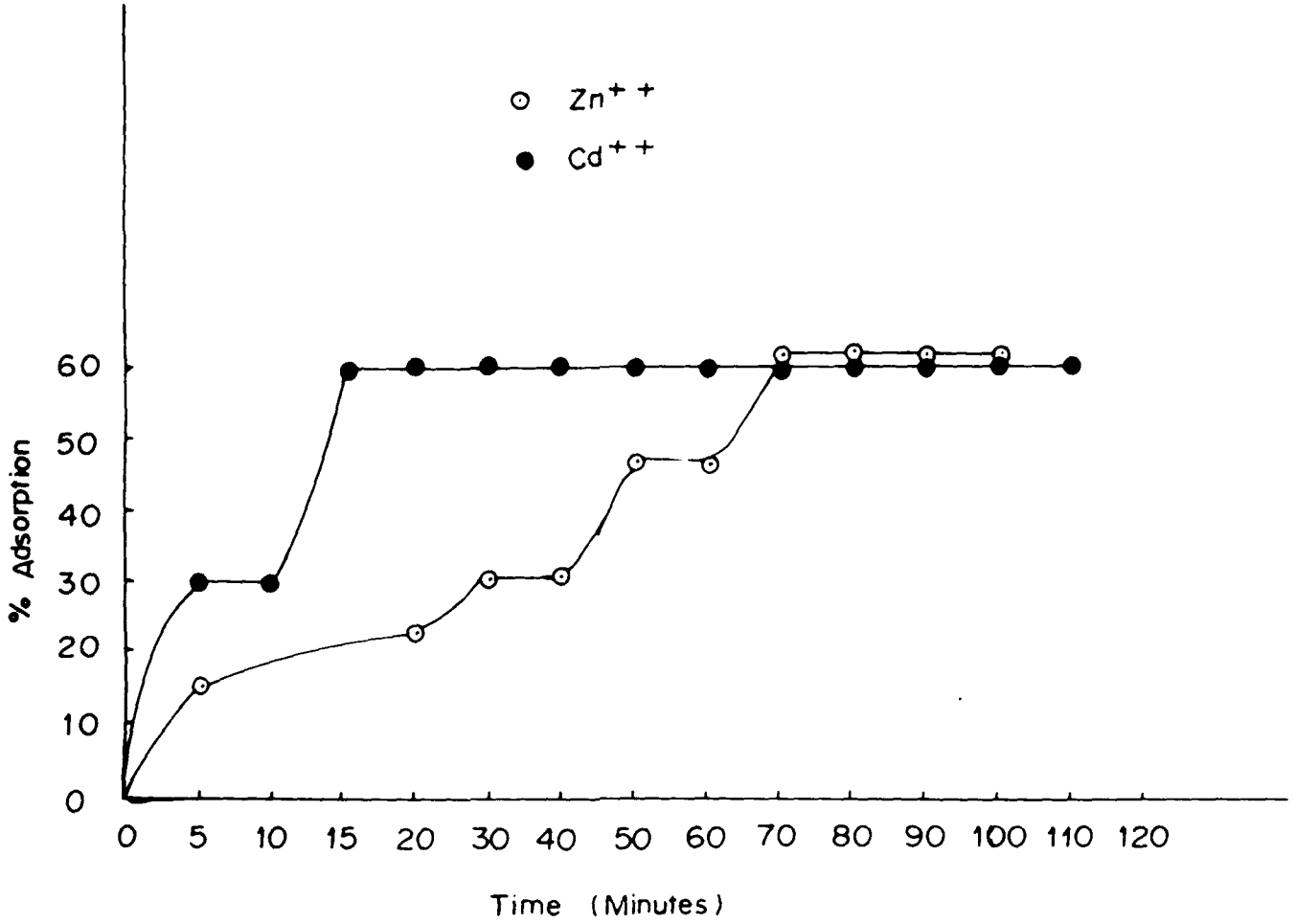

FIGURE 2.1: *Effect of time on removal of* Zn^{++} *and* Cd^{++} *by saw dust.*

RESULT AND DISCUSSION

1.5 Time of Equilibrium:

The percent adsorption of Zn^{++} and Cd^{++} was studied with time and results are shown in Fig. 2.1. It is observed that the adsorption of Zn^{++} is a multistep process and reaches to a final plateau after 70 minutes. The maximum uptake after this time is constant at a value of 61.5% adsorption. On the other hand, the behavior of Cd^{++} is entirely different from that of Zn^{++}. It shows just a two step process and the final plateau is obtained after 15 minutes where the uptake of Cd^{++} reaches to a value of 60%. Thus the adsorption of Cd^{++} on saw dust is more and faster in comparison to that of Zn^{++}. However, the time of equilibrium used in all the following studied was set to 1.5 hour for the sake of simplicity as well as to ensure the complete process of adsorption in both cases.

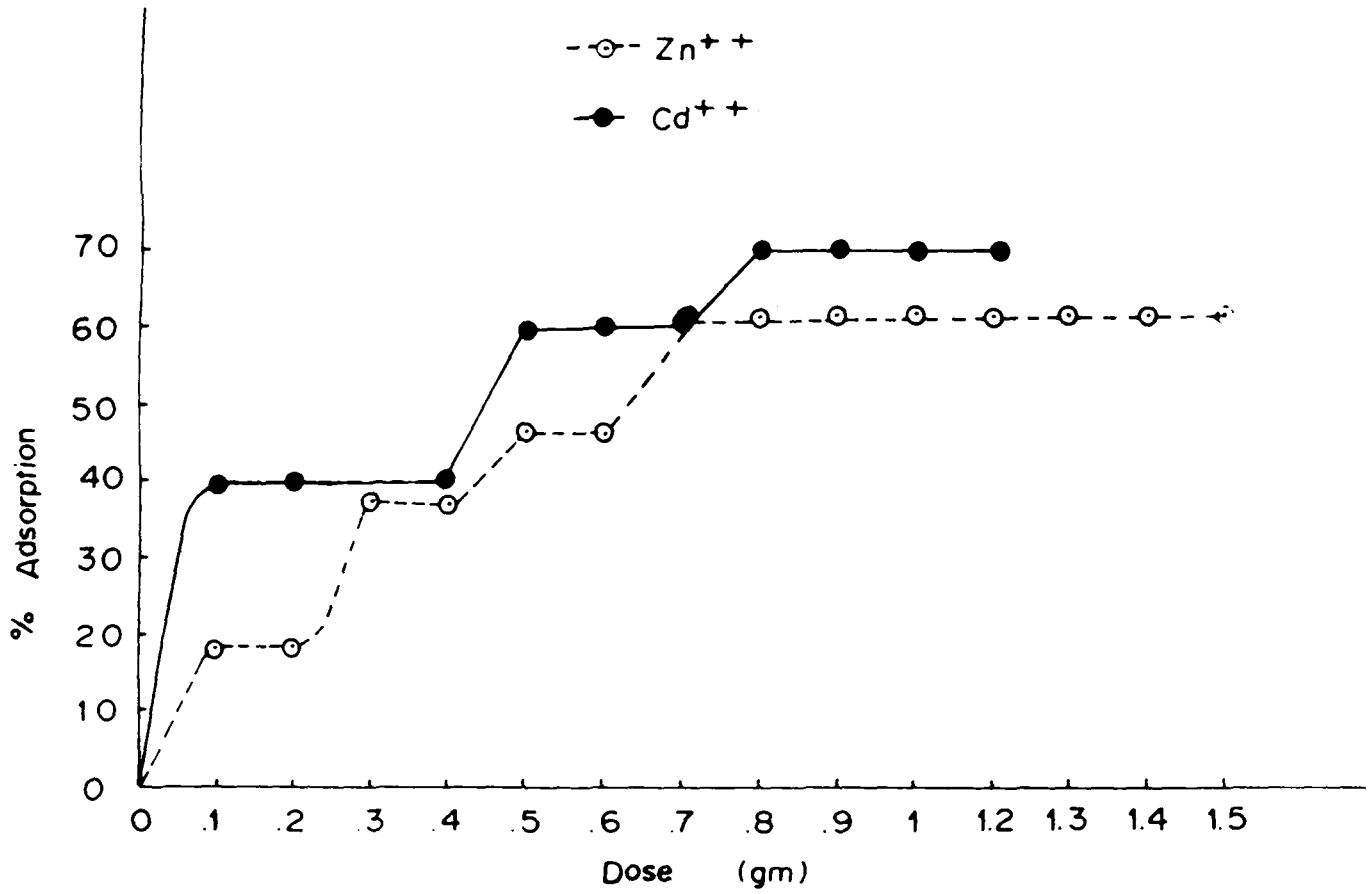

FIGURE 2.2 : Effect of dose on removal of Zn^{++} and Cd^{++} by saw dus

1.6 Effect of dose of saw dust :

The effect of the dose of saw dust on the adsorption of Zn^{++} and Cd^{++} has been depicted in Fig. 2.2. The percent adsorption increases with increase in the dose of adsorbent. But the adsorption increases in a stepped fashion. In case of Zn^{++} ions, the final plateau is attained at 62% adsorption for a dose of $\geq$ 0.7 gm of saw dust. On the other hand Cd^{++} ions show a three step adsorption process which is initially very fast as compared to Zn^{++} ions and reaches to a final plateau equivalent to 70% adsorption. This plateau observed at a dose of $\geq$ 0.8 gm of saw dust.

1.7 Effect of pH:

The effect of pH on adsorption of Zn^{++} and Cd^{++} ions are shown in Fig. 2.3. The H^{+} ion concentration seems to play an important role in

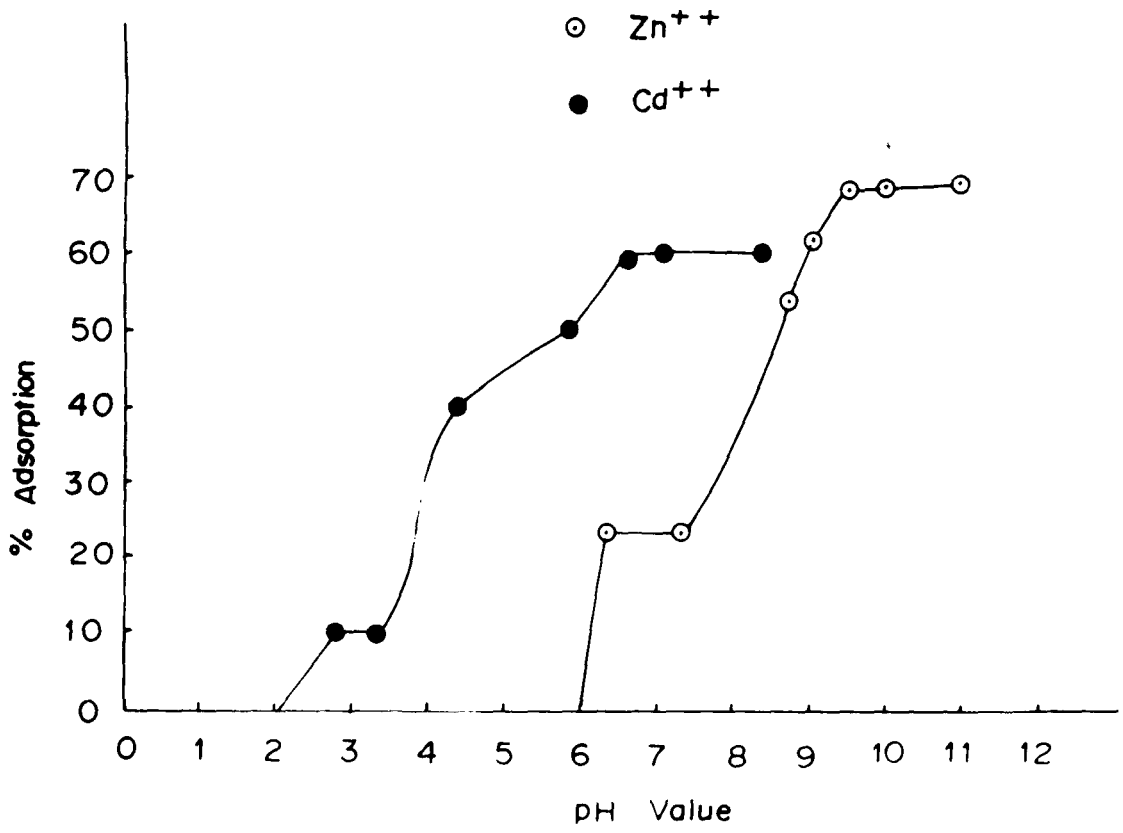

FIGURE 2.3: Effect of pH on removal of Zn^{++} and Cd^{++} by saw dust.

the adsorption of these ions. Further, the adsorption of two ions are affected in an entirely different manner by the concentration of H^{+} ions. The Zn^{++} ions show negligible adsorption upto pH 6 and the adsorption increases abruptly at a pH of 6.35. It remains constant upto pH 7.3 which is equivalent to 23% of uptake. From pH 7.3 to 9.5, it increases linearly and then reaches to a plateau which is equivalent to 70% adsorption. On the other hand the Cd^{++} ions show negligible adsorption upto pH 2. Only a 10% adsorption is observed between pH 2.8 to 3.4 and then rise, in a non linear fashion, upto 60% at pH 6.7 and it remains constant at this level at higher pH values.

The role of pH in the process of adsorption of Zn^{++} and Cd^{++} ions are entirely different and seems to follow two different types of the mechanism:

a) With increase in pH of the solution the extent of removal was found to range from zero to 60% in Cd^{++} and zero to 70% in Zn^{++}.

b) At a neutral pH value, the maximum uptake

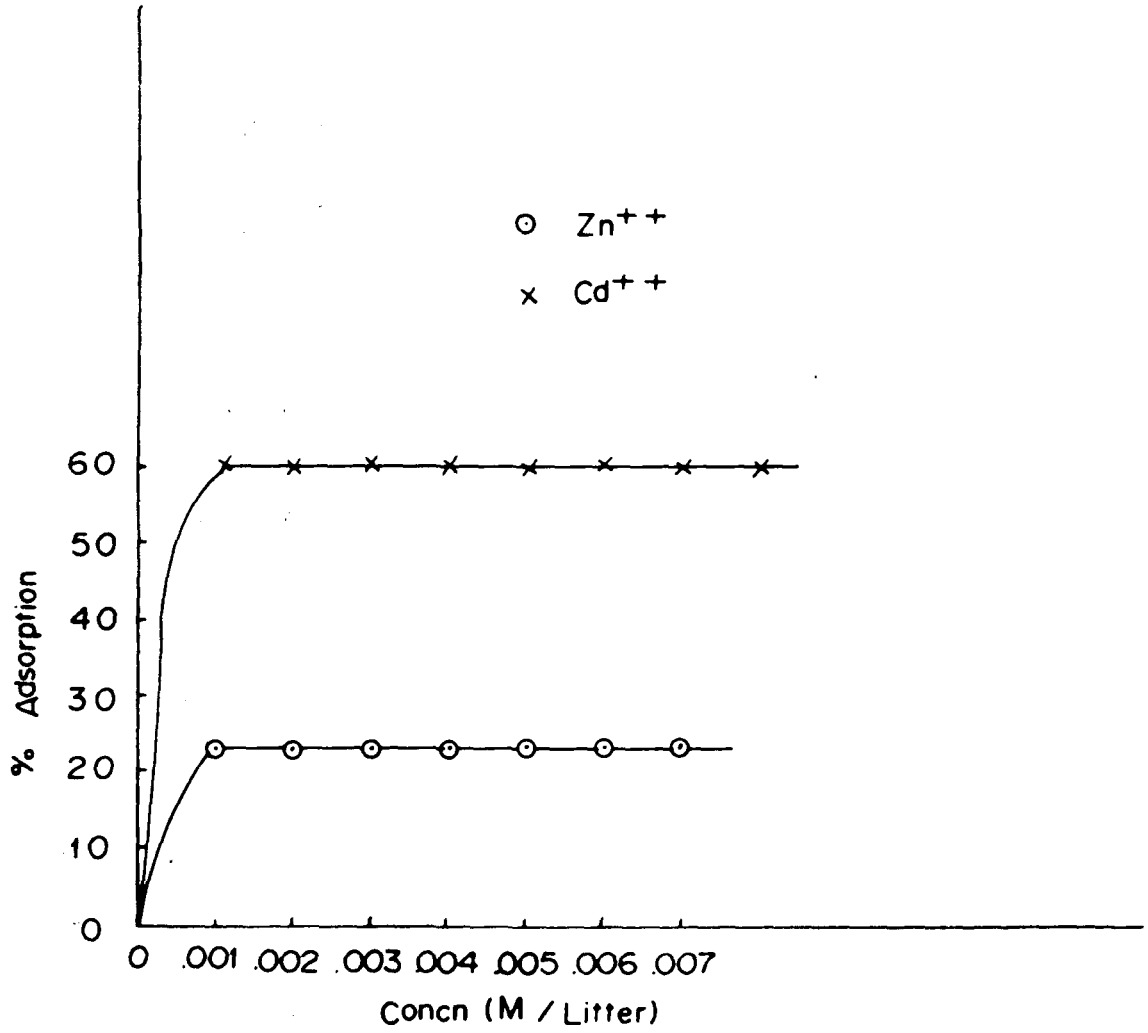

FIGURE 2.4: Effect of concentration on removal of Zn^{++} and Cd^{++} by saw dust .

of Zn^{++} is only 24% while it is upto 10% in case of Cd^{++} ions.

1.8 Effect of Concentration:

The effect of concentration on the adsorption of these metal ions are shown in Fig 2.4. The adsorption start from concentration .001 M and remains constant onwards in case of Cd^{++} as well as Zn^{++} ions. No effect of concentration has been observed in either case. However, the total adsorption in case of Zn^{++} is only 23% while in case of Cd^{++} it is upto 60%. The difference in the extent of adsorption is actually the effect of pH (as explained above) which is maintained between 6-7 to make an ideal situation.

1.9 Mechanism of Adsorption:

Actually at lower pH value, the H^{+} ions compete with metal cation for the exchange sites in the system, thereby partially releasing the latter. The heavy metal cations are completely released under circumstances of extreme acidic conditions [15]

The reason of the maximum adsorption at pH $\geq$ 6

in case of Cd^{++} are as follows. The pH of the solution, has been termed as 'Master variable' [15,16,17] in adsorption process, controlling the surface charge of the adsorbent as well as degree of ionization and speciation of aqueous adsorbates. The pH has been documented to control the surface properties of several adsorbents [18,19] In present studies maximum uptake was observed around pH 6.5.

In aqueous environments, adsorption of H^+ and OH^- ions is, thus, based on protonation and deprotonation of surface hydroxyls.

$$-ROH_2^+ \text{ ----> } -ROH + H^+ \text{ ----> } -RO^- + H^+ \qquad (6)$$

The chemical interactions of primary importance are:

(i) the interaction of solute with the surface

(ii) the interaction of the solute with the solvent

They may be classified as :

(i) **The long range columbic forces:** These forces dominate when the adsorbent surface and the adsorbate possess opposite charges in the process of adsorption.

(ii) **Short range chemical interactions:** These

forces dominate when in the process of adsorption, the surface of adsorbent is neutral or bears a charge similar to that of adsorbate.

(iii) **Surface complexation:** It is generally invoked to describe the reactions at solid-solution interface [14]. The surface hydroxides donate or accept hydrogen ions which leads to the formation of surface charge. These reactions involving molecules on the surface of the adsorbent are analogous to the solution reactions. The metal ion on the surface of the adsorbate can form complexes with ligands, just as a metal in solution does. The surface complex formation results in specific adsorption and does not depend on electrostatic attraction [20]. The maximum removal of Cd^{++} on saw dust is observed at pH $\geq$ 6.5. The variation of adsorption with change in pH of the system undertaken shows three distinct regions of interest:

(1) Between pH 2.5 - 3.5, the adsorption in this range is only 10%

(2) Between 3.5 - 6.5, there is a significant

increase in the removal of Cd^{++} with the rise in pH.

(3) Beyond pH 6.5 an adsorption edge is observed equivalent to 60% only. The possible mechanism of adsorption of Cd^{++} on saw dust is as follows:

In the first region, ion exchange mechanism may be operative due to interactions at constant charge sites.

$$Cd^{++} + 2R\ Na^{+} \longrightarrow R_2\ Cd^{+} + 2\ Na^{+} \qquad (7)$$

This type of mechanism has also been suggested by Huang and Rhoads [21]. The second region, which is greater than pH_{zpc} is very much influenced by pH. This region involves the interaction of solute with constant potential sites of the adsorbents. Apart from the weak columbic attractions the possible surface reactions accounting for specific adsorption are as follows:

Ion exchange:

$$-ROH + Cd^{++} \longrightarrow -RO^{-}\ Cd^{++} + H^{+} \qquad (8)$$

$$-ROH + CdOH^{+} \longrightarrow -RO^{-}\ Cd\ OH^{+} + H^{+} \qquad (9)$$

Adsorption:

$$-RO^{-} + Cd^{++} \longrightarrow -RO^{-} Cd^{++} \quad (10)$$

$$-RO^{-} + CdOH^{+} \longrightarrow -RO^{-} CdOH^{+} \quad (11)$$

Though both the metal ions show an almost similar adsorption behavior with the variation of pH but the effective pH ranges are entirely different (see Fig. 2.3). The pH 6-7 is the range where the adsorption of Zn^{++} starts on the other hand it is the range of maximum adsorption for Cd^{++} ions. It can be attributed to the effective hydrated ionic radii of the two metal ions which are 6 A° and 5 A° for Zn^{++} and Cd^{++} ions respectively.

1.10 Isotherms:

The related parameters for the fitting of Freundlich and Langmuir equations at different temperatures are summarized in Table 2.1 (for Cd^{++}) & 2.2 (for Zn^{++}) and isotherms plots shown in Fig. 2.5-2.6 (for Zn^{++}) & 2.7-2.8 (for Cd^{++}) respectively. The thermodynamic parameters calculated on the basis of the two models are summarized in Tables 2.3 (for Zn^{++}) & 2.4 (for Cd^{++}).

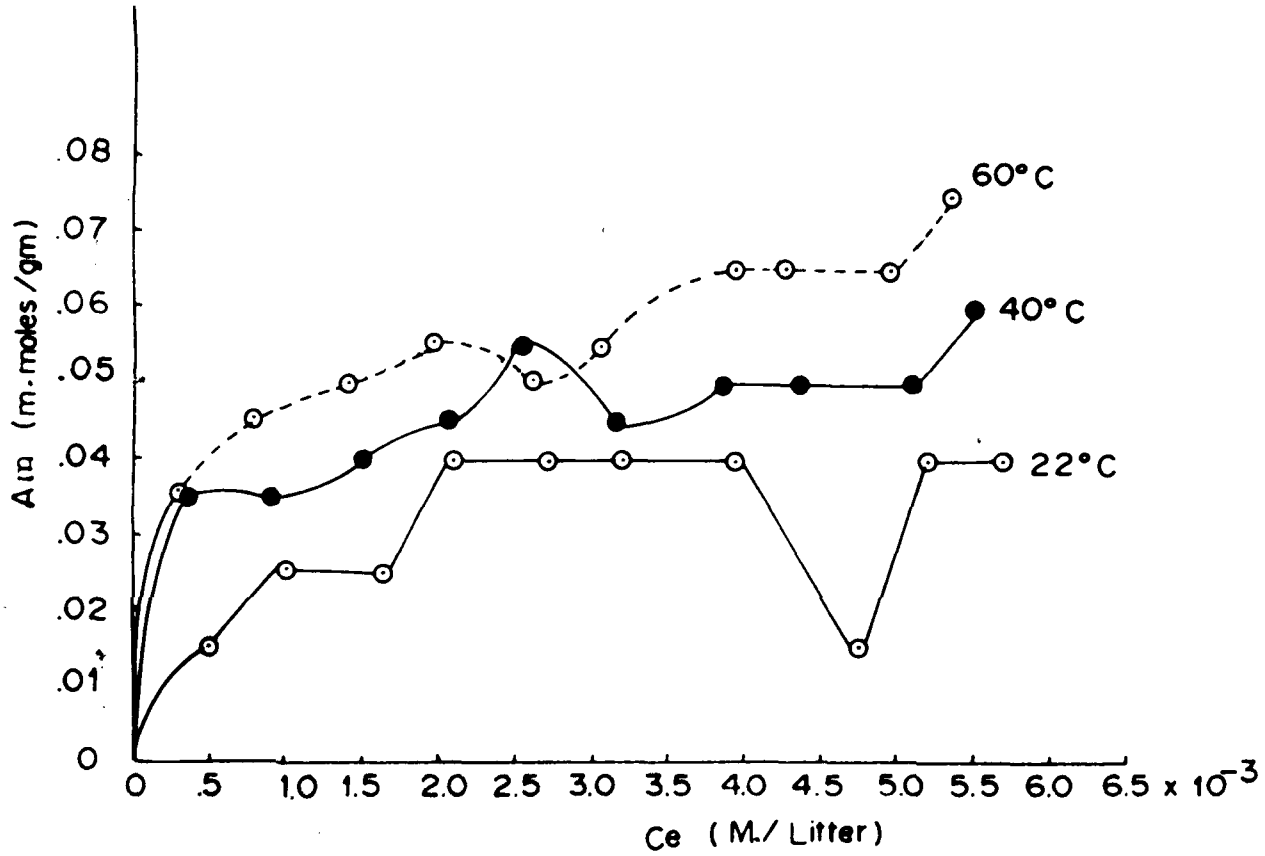

FIGURE 2.5 : Adsorption of Zn^{++} on saw dust at various temperatures

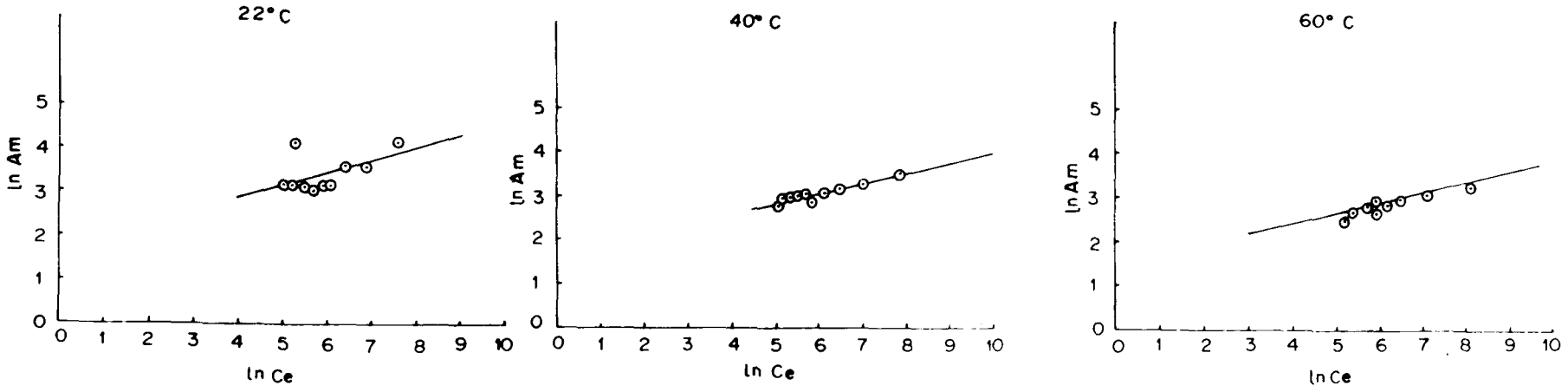

FIGURE 2.6a: Freundlich plots for the adsorption of Zn^{++} on saw dust

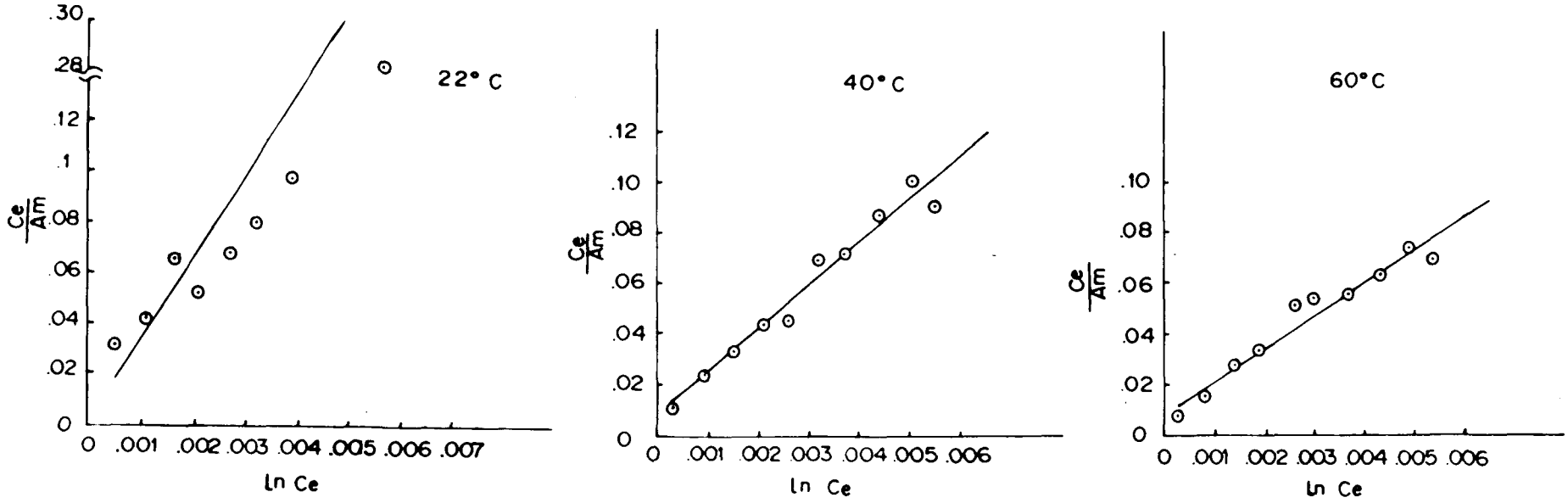

FIGURE 2.6 b : **Langmuir plots for the adsorption of Zn^{++} on saw dust .**

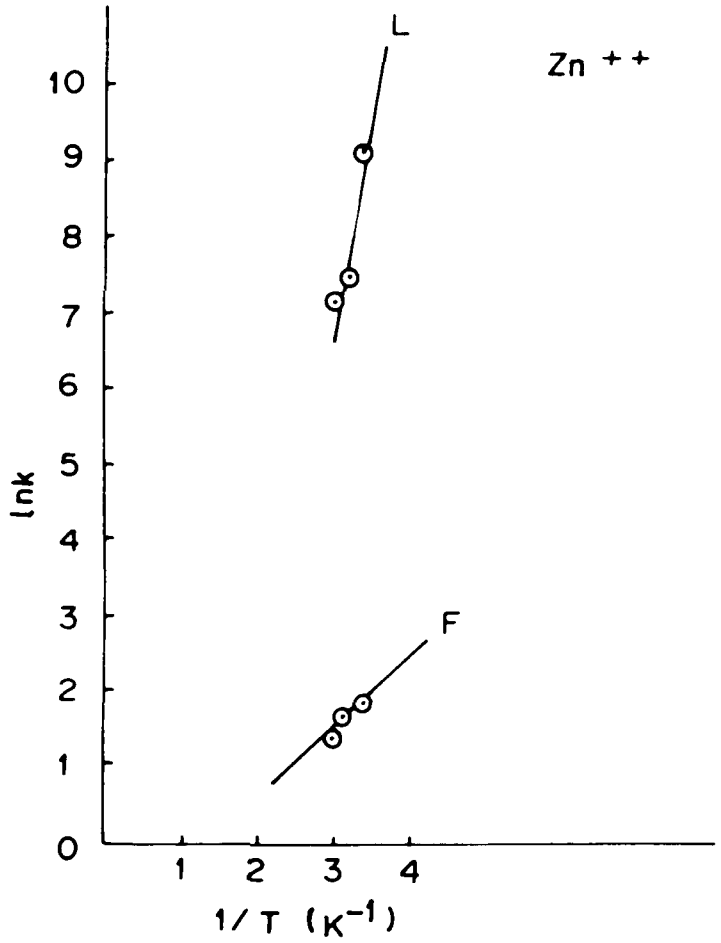

FIGURE 2.6 c : The plot of Langmuir and Freundlich constant (lnk) Vs temperature (1/T).

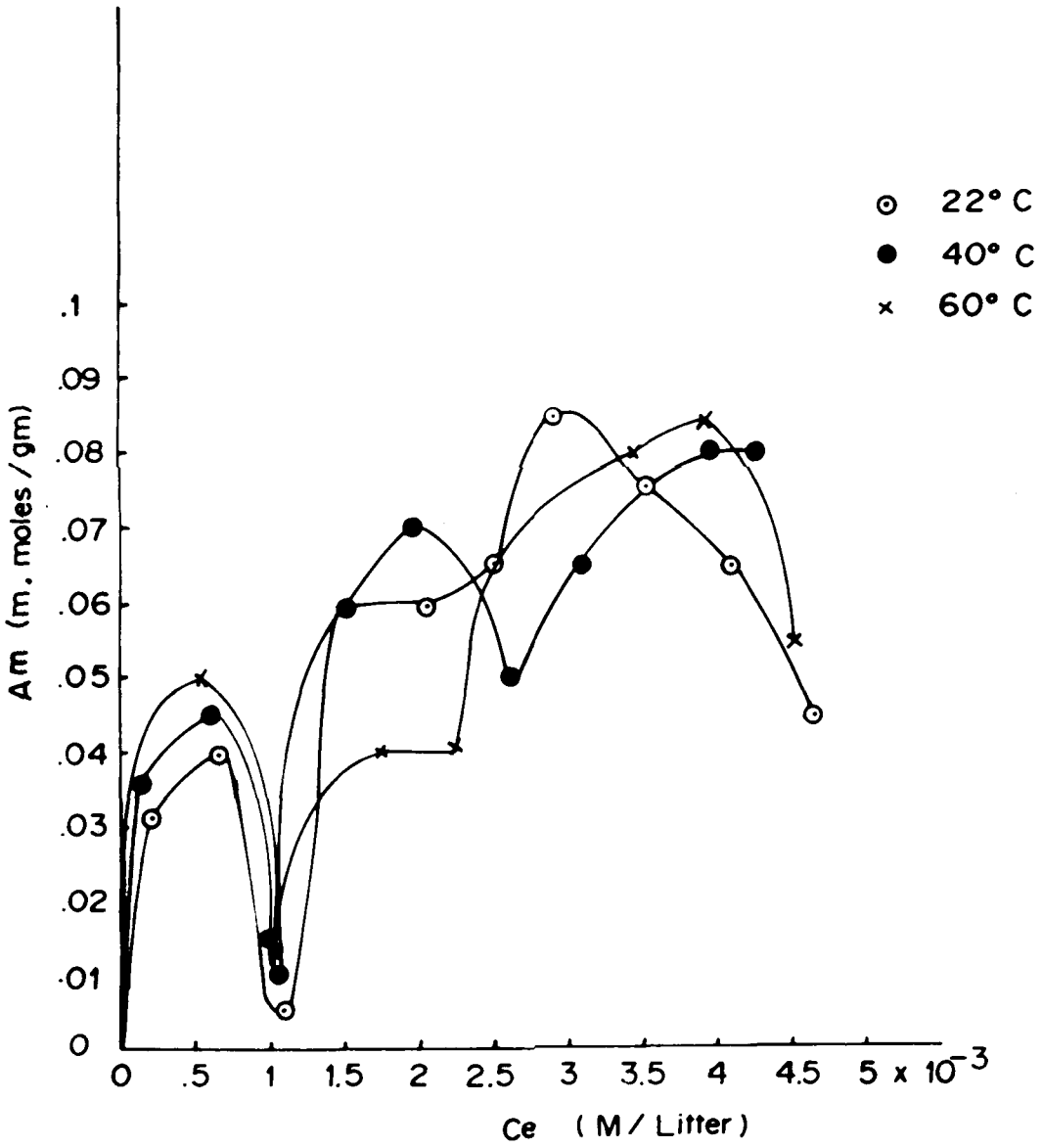

FIGURE 2.7 : The adsorption of Cd^{++} on saw dust at various temperatures .

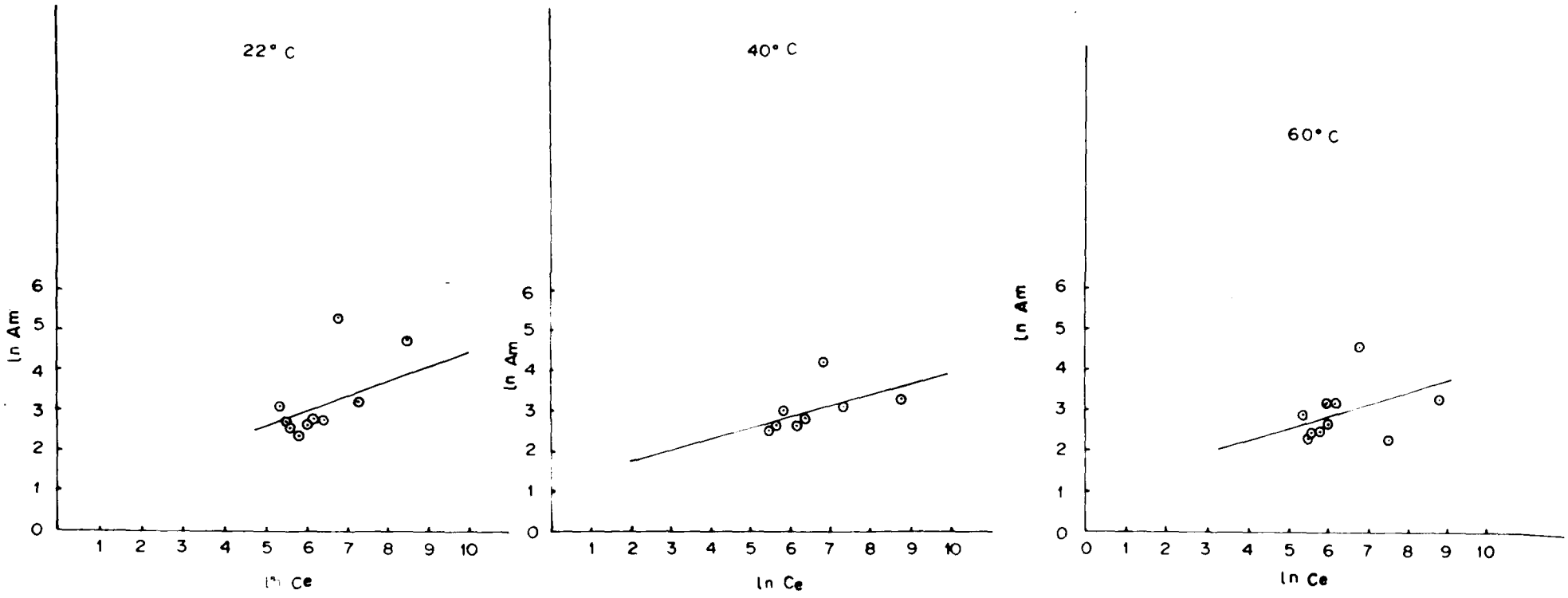

FIGURE 2.8 a : **Freundlich plots for the adsorption of Cd^{++} on saw dust .**

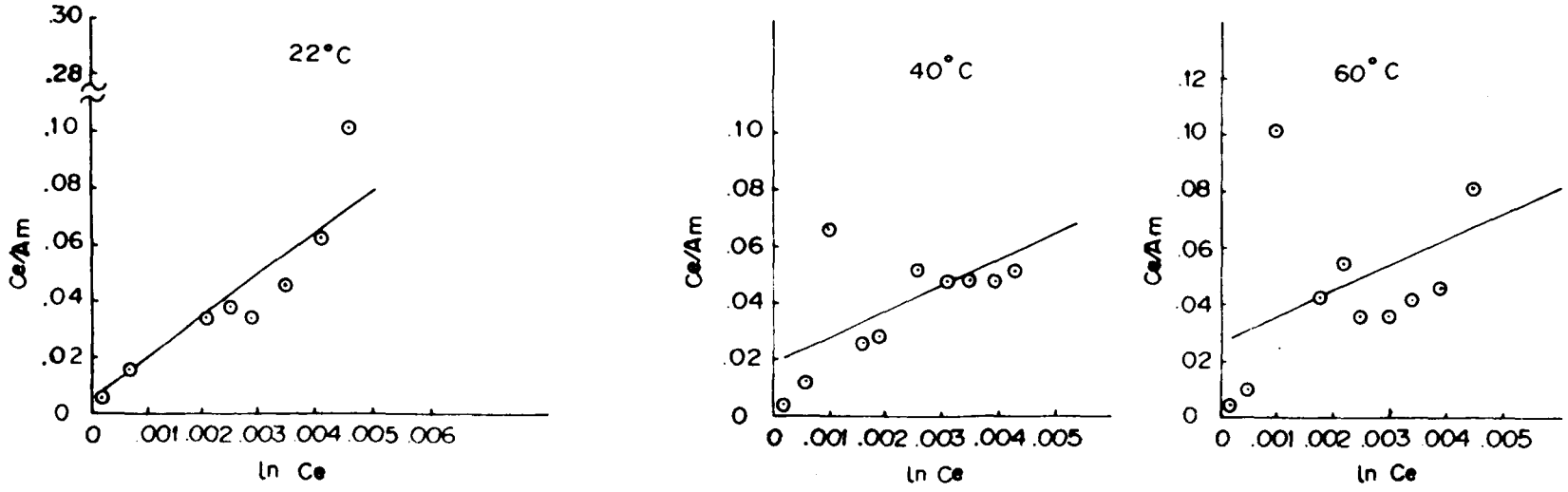

FIGURE 2.8 b : Langmuir plots for the adsorption of Cd^{++} on saw dust .

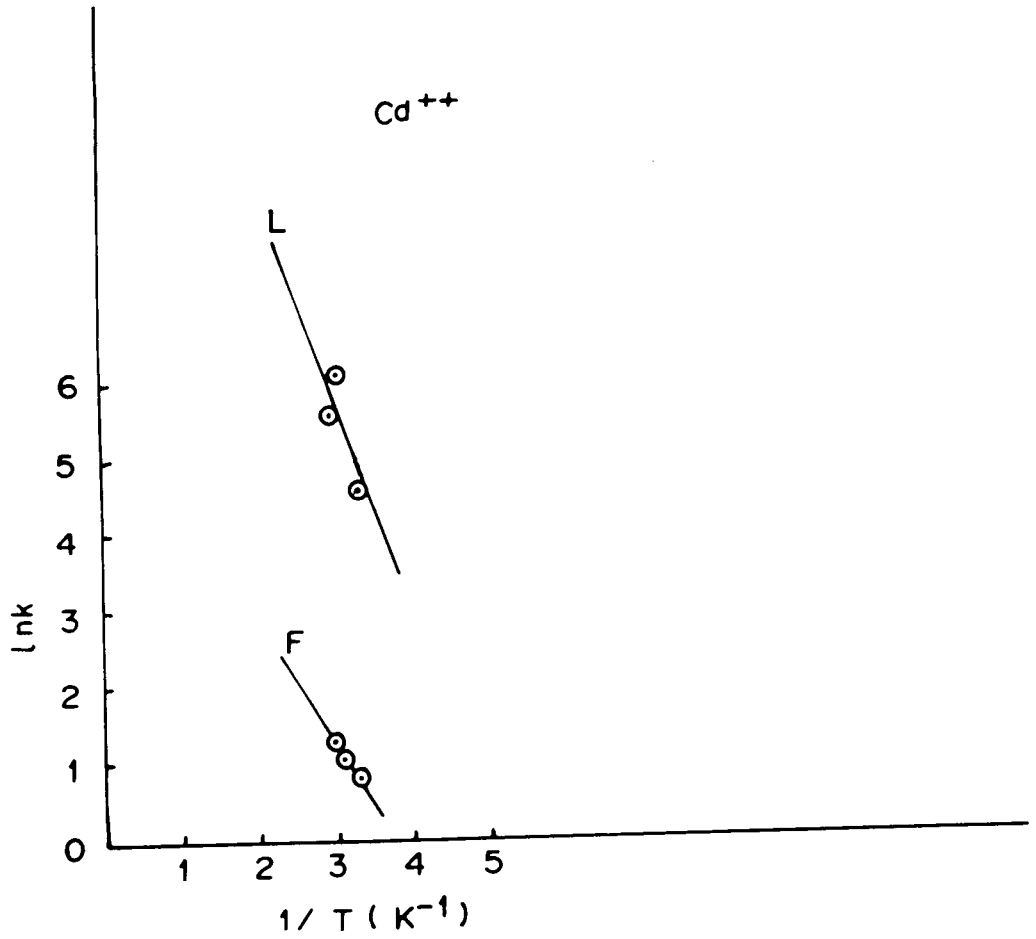

FIGURE 2.8 c : The plot of Langmuir and Freundlich constant (lnk) Vs temperature (1/T) .

Table No. 2.1

The Related Parameters for the adsorption of Cd^{++} on Saw Dust at Different Temperatures

Temp. (^{o}C)	Reg. Coeff. (R)	Freundlich Constants K	1/n	Reg. Coeff. (R)	Langmuir Constant K	b
22	0.42828	0.44409	0.36301	0.11037	0.45842	0.21330
40	0.59452	0.34016	0.29093	0.62728	0.612052	0.11539
60	0.45224	0.26432	0.26879	0.37952	0.56127	0.12757

Table No. 2.2

The Related Parameters for the adsorption of Zn^{++} on Saw Dust at Different Temperatures

Temp. (^{o}C)	Reg. Coeff. (R)	Freundlich Constants K	1/n	Reg. Coeff. (R)	Langmuir Constants K	b
22	0.52873	0.15838	0.27743	0.69598	0.91390	0.03098
40	0.92848	0.17689	0.22437	0.98231	0.74487	0.05907
60	0.95439	0.22779	0.23193	0.97807	0.71944	0.07677

The adsorption of Zn^{++} between pH 6-7 follow both Freundlich as well as Langmuir type isotherm. However, the Langmuir equations is better obeyed by the system than the Freundlich one as is evident from the values of regression coefficients which are very close unity at 40 and 60 °C whereas they are far from unity in both the cases at 22 °C.

The Freundlich type adsorption isotherm is indicative of surface heterogeneity of the adsorbent while Langmuir isotherm hints towards its surface homogeneity. This leads to the conclusion that the surface of saw dust is made up of small heterogeneous adsorption patches which are very much similar to each other in respect of adsorption phenomenon.

The overall adsorption increases with the increase in temperature at all the concentrations and no cross over is seen, that is, there is no reversal in the process of adsorption or selectivity. However, at all the temperatures, a minima is seen. At $22^{o}C$ corresponding to Am= .015 m moles/g at Ce = 4.75×10^{-3} M. At 40 and

Table No. 2.3

The Thermodynamic Parameters for the adsorption of Zn^{++} on Saw Dust at Different Temperatures

Temp. (^{O}C)	Freundlich Adsorption Isotherm				Langmuir Adsorption Isotherm			
	lnK	ΔG	ΔS	ΔH	lnK	ΔG	ΔS	ΔH
22	-1.84306	1.08034	0.00266	1.865 Kcal/K/mol	9.13909	-5.35702	-0.01577	-10.0083 Kcal/K/mol
40	-1.73254	1.07752	0.00252		7.44874	-4.63260	0.01717	-
60	-1.47960	0.97901	0.00266		7.19442	-4.76034	0.01576	

Table No. 2.4

The Thermodynamic Parameters for the adsorption of Cd^{++} on Saw Dust at Different Tempratures

Temp. (^{O}C)	Freundlich Adsorption Isotherm				Langmuir Adsorption Isotherm			
	lnK	ΔG	ΔS	ΔH	lnK	ΔG	ΔS	ΔH
22	-0.81188	0.47589	-0.01065	-2.666 Kcal/K/mol	4.58429	-2.68715	0.02711	5.3100 Kcal/K/mol
40	-1.07852	0.67077	-0.01065		6.12052	-3.80654	0.02913	
60	-1.33085	0.88058	-0.01065		5.61271	-3.71377	0.02710	

$60^{O}C$ the minima is observed at Ce = 3.15 x 10^{-3}M and Ce=2.6 x10^{-3} corresponding to Am = 0.045 and .05 m moles/g respectively. **The overall behavior of the system indicates that it is a multilayer endothermic adsorption process.** This statement contradicts to the earlier statement that Langmuir adsorption isotherm is better obeyed. It can be justified as follows:

(1) The multilayer adsorption process is not possible in case of Langmuir model. It is only possible in Freundlich adsorption model where the surface of the saw dust is assumed to be made up of heterogeneous patches which are homogenous in themselves (As explained above)

(2) The application of van't Hoff type equation for the calculation of thermodynamic parameters (Tables 2.3 & 2.4) shows that the Enthalpy of adsorption is positive in case of Freundlich adsorption model whereas it is negative for the Langmuir one. The positive Δ H value of the former model corresponds to endothermic process which we have observed. Hence it is proved that

Freundlich adsorption model is obeyed in the adsorption of Zn^{++} on the saw dust.

To find out the reason of appearance of the minima in the adsorption isotherm, the pH of the system is noted and it is found to be 5.8, which is less than 6.5, a value to which the system was preset by adding NaOH. The ion exchange seems to be possible mechanism of this minima. With the increase in concentration, the aggregation of the metal ions at the surface of the saw dust increases which results to the exchange reactions with the already protonated sites, resulting thereby an increase in H^{+} concentration and hence a decrease in pH. The latter effect decreases the adsorption of the metal ions leading to a minima in the adsorption isotherm. With the rise in temperature, this minima shifts to a lower value of the concentration of metal ions. The increased temperature increases the aggregation of ionic species and hence brings about the ion exchange process at lower equilibrium concentration.

The adsorption studies were also conducted in

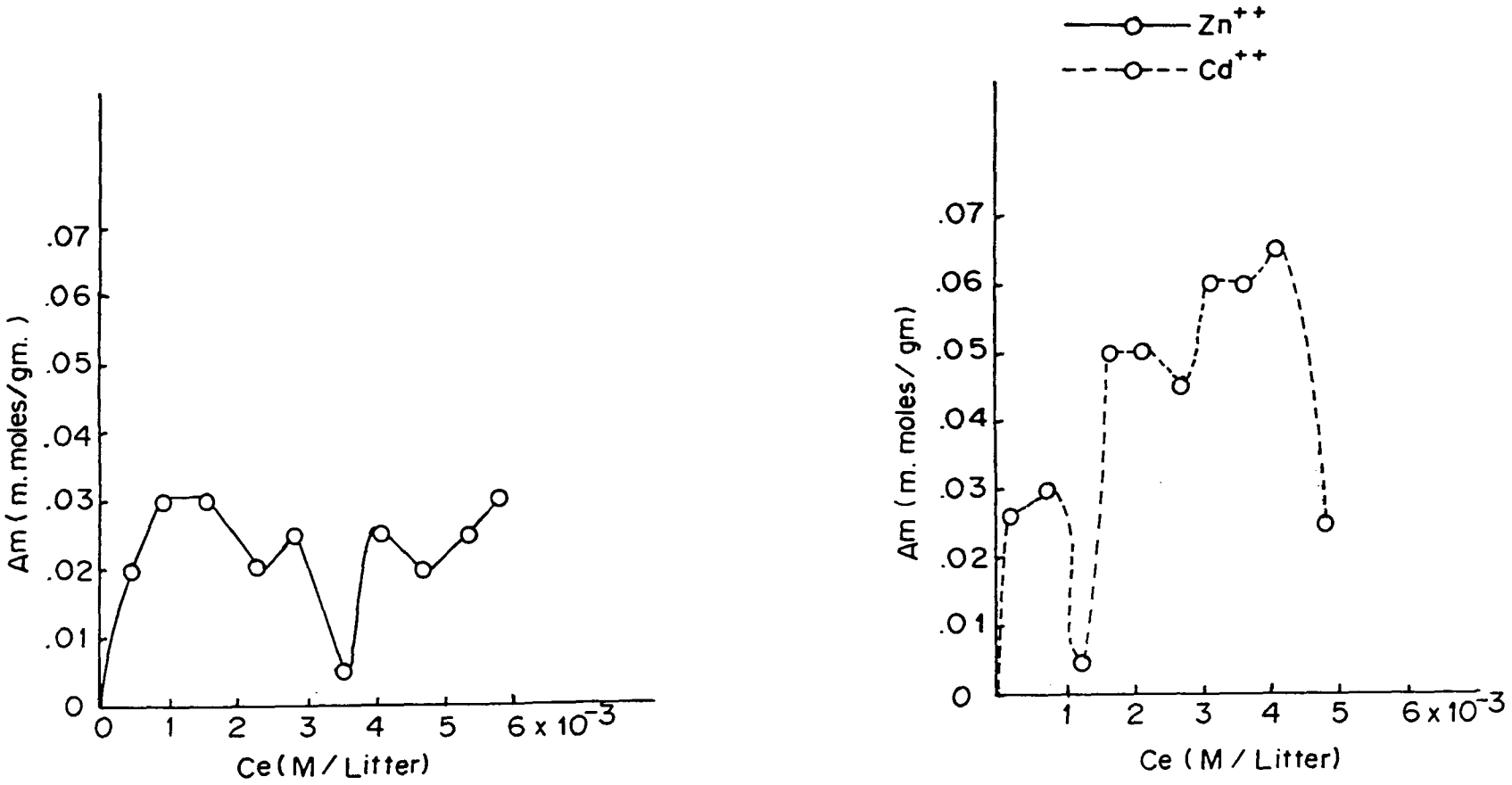

Figure 2.9 : Effect of NaCl on removal of Zn^{++} and Cd^{++} by saw dust at 40° C.

presence of 0.1 M NaCl at $40^{o}C$ only. Both the metal ions (Zn^{++} , Cd^{++}) show a minima at Am=0.005 m. moles/g corresponding to Ce= 3.6×10^{-3} and Ce= 1.2×10^{-3}M respectively (see Fig. 2.9). These values of Am are very low as compared to the values noted in absence of NaCl. The reason of this minima has already been discussed.

Adsorption of Cd^{++} on saw dust at different temperatures is shown in Table 2.1 . It is clear from the values of regression coefficients that neither it follows Langmuir nor Freundlich type isotherm. Initially, the extent of adsorption increases with the rise in temperature which indicates that the process is endothermic. After an equilibrium concentration of 0.5 M, a cross over in adsorption isotherms is observed which result to a decrease in the extent of adsorption at $60^{o}C$ resulting thereby to a minima at Ce = 1 M. However, the adsorption at $40^{o}C$ and $22^{o}C$ becomes almost equal between Ce = 0.6 to 2 M. With the increase in equilibrium concentration so many cross overs are observed among the three adsorption

isotherms and finally the order of the extent of adsorption becomes 40 > 22 > 60^{o}C.

According Giles classification [22] the adsorption of Cd^{++} on saw dust shows 'S' type isotherm. This class of adsorption isotherm is indicative of the composite isotherm where there is a competition between the solute and solvent molecules for the adsorption on the adsorbent . The following may be the possible mechanism of over all process of Cd^{++} adsorption.

Initially the adsorption of Cd^{++} ion at all the temperatures occur in the unhydrated form i.e. the dehydration of both the ions and the adsorption site occurs first and then they get adsorbed. On increasing the concentration of the ions in solution, the aggregation of these ions increases on the surface leading to their access to the less accessible sites. This tends to an increase in the adsorption through the opening of the pores of adsorbent. The latter effect facilitate the entry of water molecules too into the pores. On the entry of water, the adsorbed ions/sites gets hydrated

leading to a decrease/reversal in the extent of adsorption. Thus it causes a minima in the adsorption process.

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